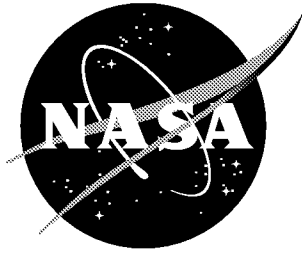# Stretch-Oriented Polyimide Films

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April 2000

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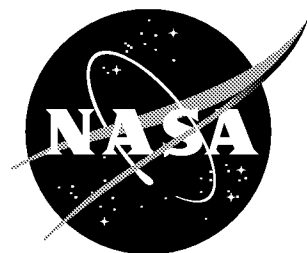
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Abstract

Two thermoplastic polyimides – one amorphous, the other crystallizable -- were subjected to isothermal stretching just above their glass transition temperatures. Room-temperature strengths in the stretch direction were greatly improved, and, moduli increased up to 3.6-fold. Optimum stretching conditions were determined.

Introduction

Polymer films are useful as transparent windows, as flexible structural elements, as electrical substrates, and as vapor barriers. Their optical, electrical, mechanical, and barrier properties can often be improved by in-plane film orientation brought about by stretching. Textile fibers, too, are highly dependent on drawing and annealing to optimize their strengths and stiffnesses.

It is of interest, therefore, to explore the effects of drawing on thermoplastic aromatic polyimides, a class of thermally-stable, radiation-resistant polymers. Previous thermal deformation experiments[1,2] with various polyimides showed that some of them underwent strain-induced crystallization when they were heated slowly under load. In the studies reported here, various stretch ratios, stretching rates, and stretching temperatures were employed in an effort to optimize the stiffness of uniaxially-drawn films. Isothermal stretching was applied to a polyether imide, LARC™-IA, and to a closely-related copolymer, LaRC™-IAX.

Experimental

LARC™-IA[3,4] is a nominally amorphous polyimide with a glass transition temperature of 241°C. Poly(amic acid) precursor solution (30% in N-methyl pyrrolidinone) was obtained from Imitec, Inc., Schenectady, New York. Molecular weight was controlled during the synthesis by offsetting the stoichiometry 3% in favor of the diamine; the chains were capped with phthalic anhydride. Films were cast on soda-lime glass plates, dried for several days at room temperature

under low humidity, and cured for 1 hour each at 100°, 200°, and 300°C. To make LARC™-IAX, 10% of the diamine is replaced with p-phenylene diamine.

Stretching was performed in an air-circulating oven using dead-weight loading.[1] Length change was monitored using a long-stroke displacement transducer attached to the weight. Tensile tests on drawn films were performed at room temperature with a gauge length of 3.8 cm and a crosshead speed of 0.5 cm/min; strain was calculated from crosshead displacement.

Differential scanning calorimetry (DSC) was performed at 20°C/minute in air using a Shimadzu analyzer.

Results and Discussion

LARC™-IA

If a suitable constant load is applied to a LARC-IA specimen in the temperature range 240-280°C, the film elongates readily initially, but at a certain strain, the stretching slows spontaneously. This "natural" draw ratio at which stretching slows ranges from 300% to 750%, depending on the temperature and load (Figure 1). Similar behavior is seen in PET (polyethylene terephthalate) fibers and films,[5,6] and is attributed to strain-induced crystallization. The self-limiting character of the deformation makes the material quite forgiving in terms of process variations, and allows zone-drawing[7] to be conducted quite easily[8].

Alternatively, the extent of stretch can be controlled by stopping the deformation short of the "natural" draw ratio. The moduli of the stretched films are substantially higher than that of the as-cast material. Representative tensile data are compared in Table I. As might have been expected, larger strain seems to produce a higher modulus.

Table I

Effect of Strain on room-temperature modulus
(Stretching performed at 250 °C)

Final Strain	Average Strain Rate, Sec^{-1}	Room Temperature Modulus E, GPa (in stretch direction)
Unstretched	--	2.2
4.0	0.28	5.9
5.0	0.26	7.0

Besides the total strain, two other stretching variables, the strain rate and temperature, also affect the properties of the stretched film. With our constant-load apparatus, strain rate could only be controlled indirectly by varying the applied engineering stress or the temperature.

Considering first the effect of stress, Figure 2 shows raw data at three different stress levels. Note that a logarithmic scale is needed for the abscissa; changing the stress by a factor of three brought about almost a thousandfold change in the experiment times. Each experiment was replicated three times to indicate the degree of reproducibility.

Although a detailed study of the rheology of this process is beyond the scope of this report, it is of interest to compare this imide to more conventional commodity polymers. Elongational flows can take a very long time to reach steady state[9]. It is customary, then, to plot the instantaneous elongational viscosity (also known as the "stress growth function") against time. This has been done even in cases where the strain rate is not constant[10] (as is the case in the present experiments). Data from Figure 2 are replotted this way in Figure 3.

As expected, the viscosity is an increasing function of time. At times below one second the curves for the three stress levels seem to converge to an elongational viscosity of about 10^6 Pa sec. This is comparable to values reported for other thermoplastics[9]. At longer times, the curves in Figure 3 undergo a change in slope; the upturn happens earlier at higher strain rates. This feature, too, has been seen in polyethylene terephthalate[11]. The low-rate viscosity shows a modest temperature dependence, rising to ~3 MPa sec at 245°C and falling to ~0.4 MPa sec at 280°C.

Specimens made by the processes outlined in Figure 2 were tested to failure at room temperature. The results are shown in Table II. It is clear that a high strain rate is advantageous in producing a greater degree of orientation (and thus a higher modulus). It is thought that this is because the desired strain-induced chain orientation is in competition with chain relaxation occurring at the stretching temperature[12].

Table II

Effect of Strain Rate (250°C, $\varepsilon = 3.5$) on Room Temperature Tensile Properties

Average Strain Rate, Sec^{-1}	E, GPa
--	2.87
0.004	3.29
0.21	6.54
3.7	8.79

With some polymers, a rapid quench is helpful in maintaining the orientation produced by the stretching. To test this for LaRC-IA, a series of films were maintained under load (no stop) for various periods of time after the apparent cessation of stretching. There was no discernable trend in room temperature modulus upon varying the hold time from 30 seconds to 570 seconds at 250°C.

Synthetic textile fibers are often "heat-set" (annealed under tension) to reduce the amount of shrinkage they undergo when subsequently heated. Attempts to anneal our stretched films at constant length were unsuccessful: the films always broke. A clamping apparatus was therefore designed that allowed the films to shrink slightly during annealing but maintained some load by means of a moderately stiff spring in series with the film. Films annealed this way at 260-280°C for 30-60 minutes showed, in addition to a melting endotherm near 320°C, an additional DSC melting peak close to the annealing temperature. The total heat of melting was often less than that for a well-oriented film, however, so the mechanical properties were not determined.

The effect of stretching temperature is illustrated in Table III. At the lower temperatures, it was hard to produce a high rate of strain, so modulus was not optimum. The highest temperature produced a lower-modulus (and presumably less-oriented) film. Although the stretching rates were comparable in the 260° and 280° experiments, it seems apparent that chain relaxation is rapid relative to the experiment time at stretching temperatures above 260°C.

Table III

Effect of Stretching Temperature on Room Temperature Modulus of Oriented Film
(ε=3.5)

Stretching Temperature	E, GPa
245	6.8
250	6.0
260	9.1
280	4.8

The maximum room-temperature modulus in the stretch direction was three times that of an unstretched film. Such highly-oriented films are, of course, anisotropic. When failed in tension, they fibrillated, splitting along the stretch direction. This is in contrast to the less-oriented films, which broke straight across.

LARC™-IAX

Experiments with LARC-IAX were conducted in the same way as those already described. It is worth noting, however, that in contrast to LARC-IA, the copolymer LARC-IAX did not seem to

crystallize during stretching. The films remained clear and no films were observed to stop straining on their own.

Figure 4 illustrates the effect of strain at the lowest stretching temperature. The same load was used for all six specimens, so strain rates were comparable; a stop was used to define the maximum strain. Similar trends were seen with 250°C and 260°C stretching. As was observed in the experiments on LaRC-IA, higher strain rates increased the moduli of stretch-oriented films; Figure 5 is an example.

In order to summarize the relative importance of the three variables strain, ε; log (strain rate); and temperature, moduli resulting from a total of 22 different sets of stretching conditions were fitted by simple linear regression, giving the equation

$$(E, GPa) = 55.47 + 1.47\ (\varepsilon) + 1.16\ (\log\ (d\varepsilon/dt,\ sec^{-1})) - 0.20\ (t,\ °C).$$

All coefficient estimates were significant (P<0.02), but a fair amount of scatter remained ($R^2 \cong 0.6$). The regression equation should not be taken too literally because some stretching conditions were represented by only a single film, and interactions between the variables were not modeled. It does suggest that the observed maximum modulus (16.1 GPa) is close to the best result one could hope for over the range of parameters accessible for study (i.e. $T \geq 240°C$, $\varepsilon \leq 5$, and strain rate $\leq 10\ sec^{-1}$).

Comparisons among films produced under a wide range of conditions showed that increased moduli were accompanied by significant decreases in room-temperature strain-to-break (Figure 6). The tensile strengths, however, remained far above that of the unstretched film (Figure 7).

Summary and conclusions

Thermoplastic polyimides were shown to behave in many ways like more familiar commodity polymers. Stretching improved moduli by factors of 3 to 6.5 in the machine direction, and was sometimes accompanied by strain-induced crystallization. Guidelines for process optimization were obtained.

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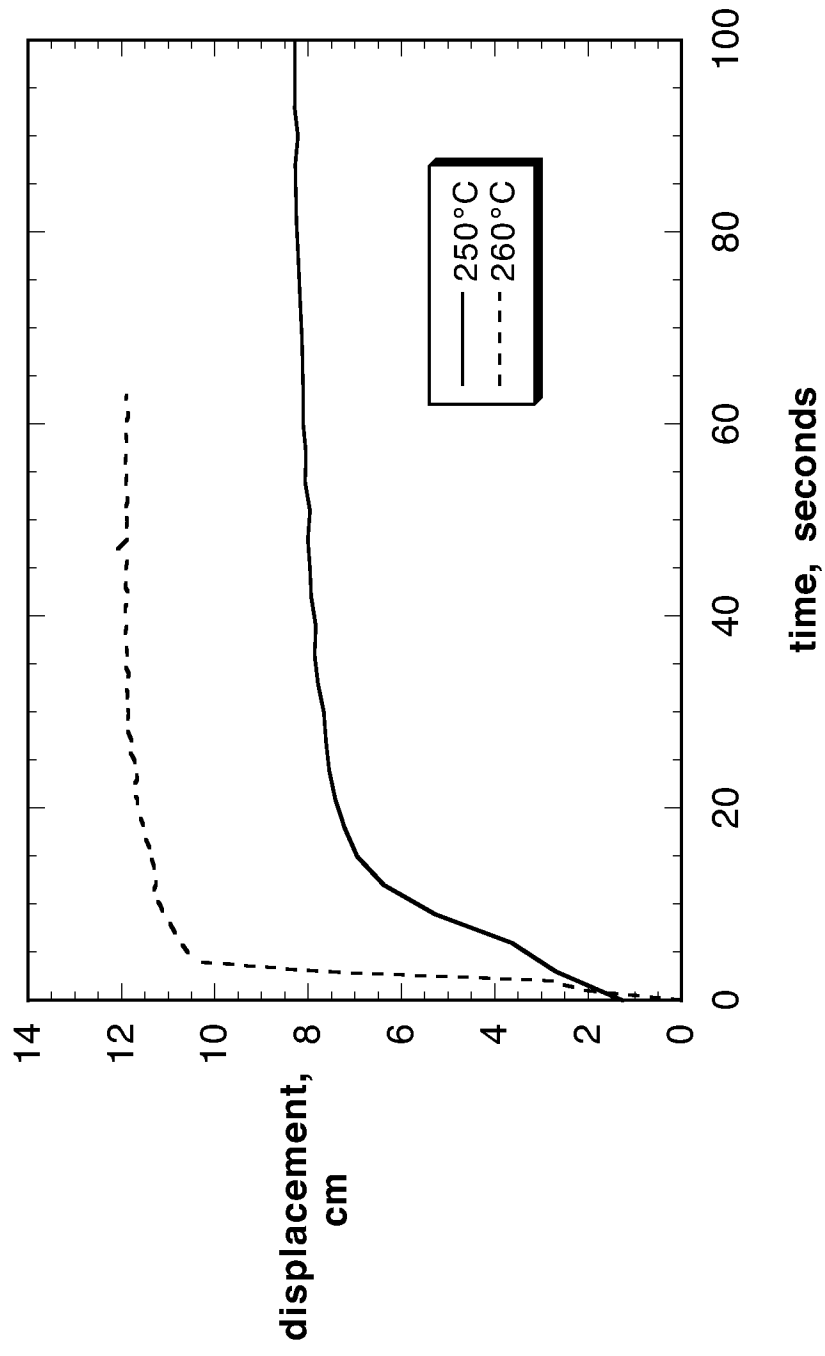
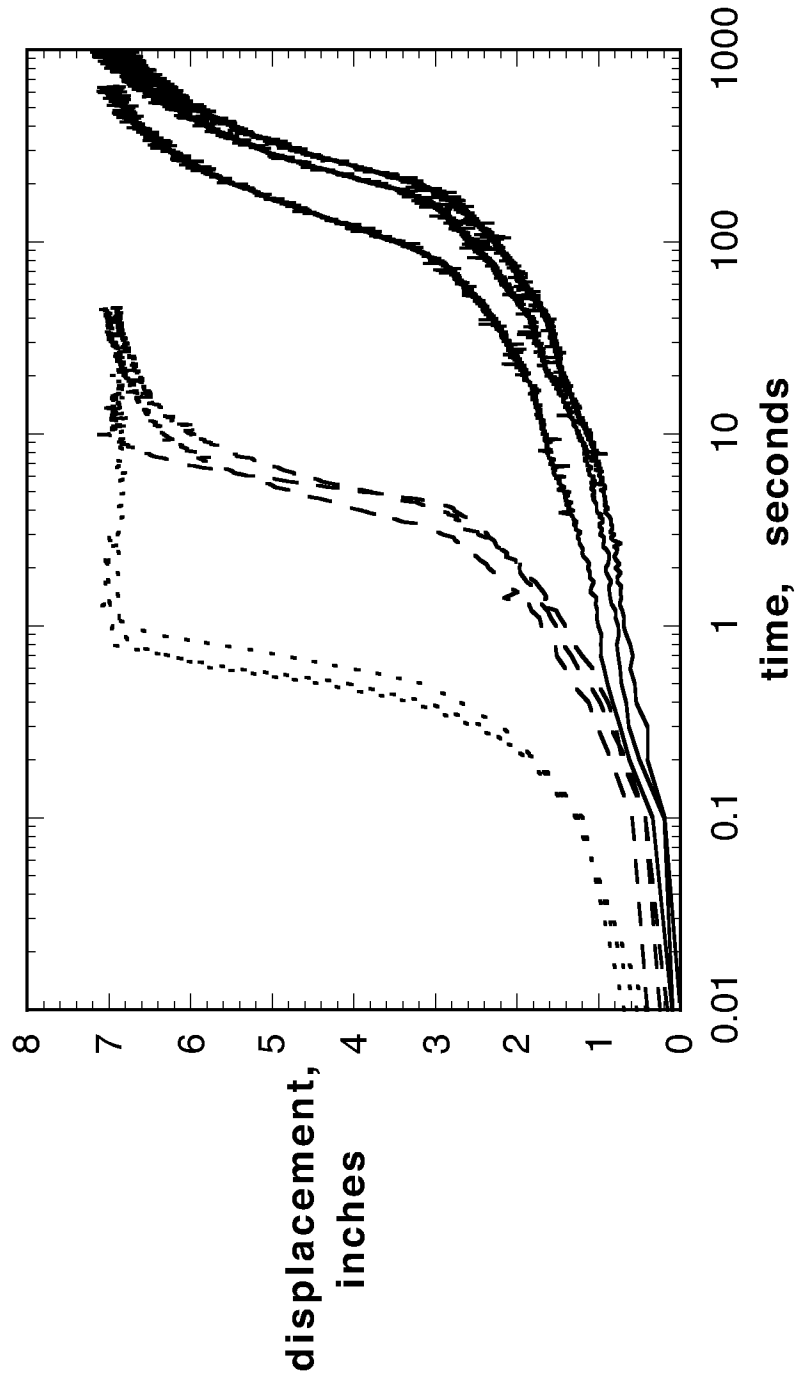Figure 1. Unconstrained uniaxial deformation of 3.8-cm LaRC$^{\text{TM}}$- IA specimens under 3 MPa load.

Figure 2. Stretching of LaRC™–IA at 250 °C and three different stress levels: 2 MPa (solid lines), 3.5 MPa (dashed lines), and 6 MPa (dotted lines). Deformation was stopped at a strain of 3.5. [1 inch = 2.54 cm].
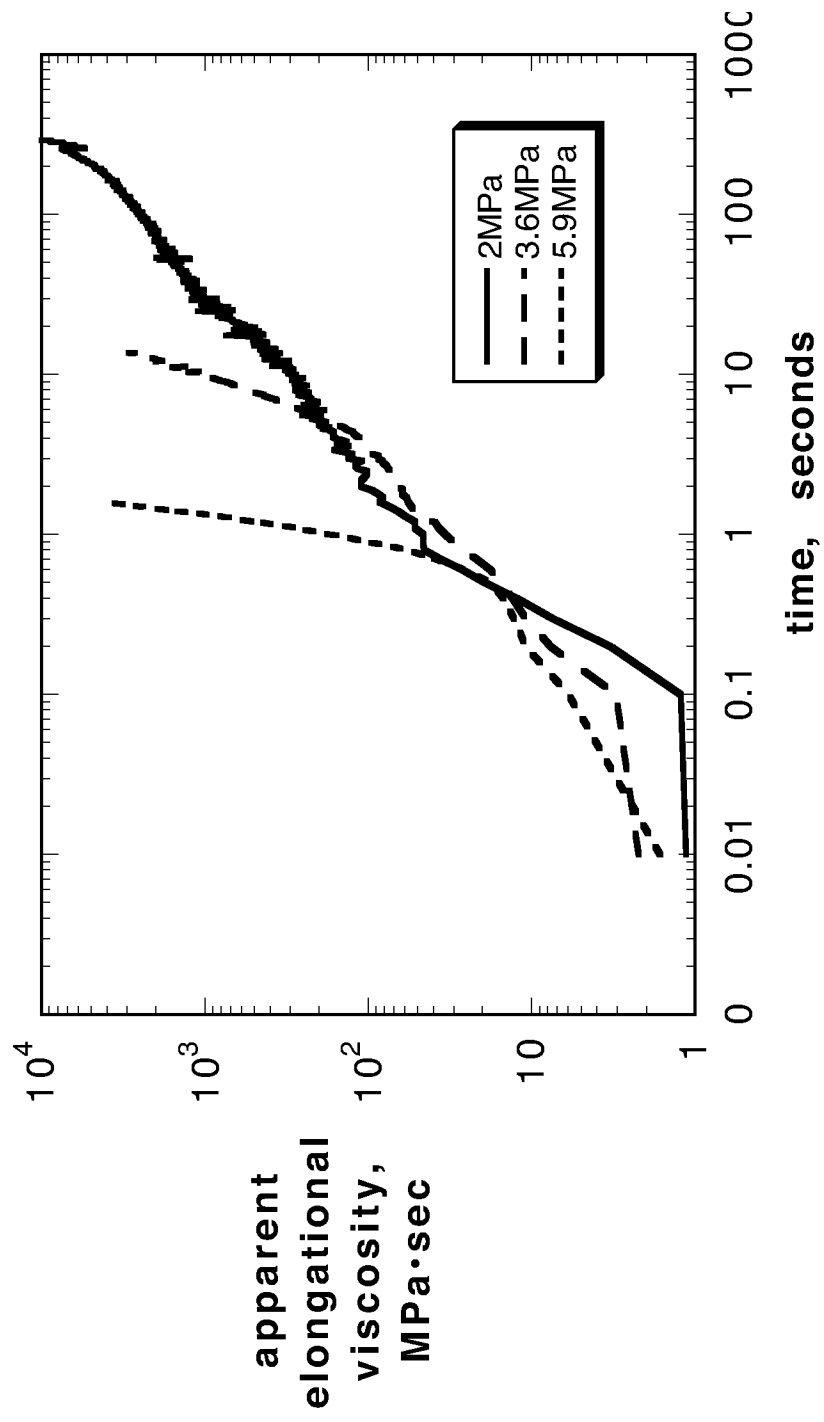
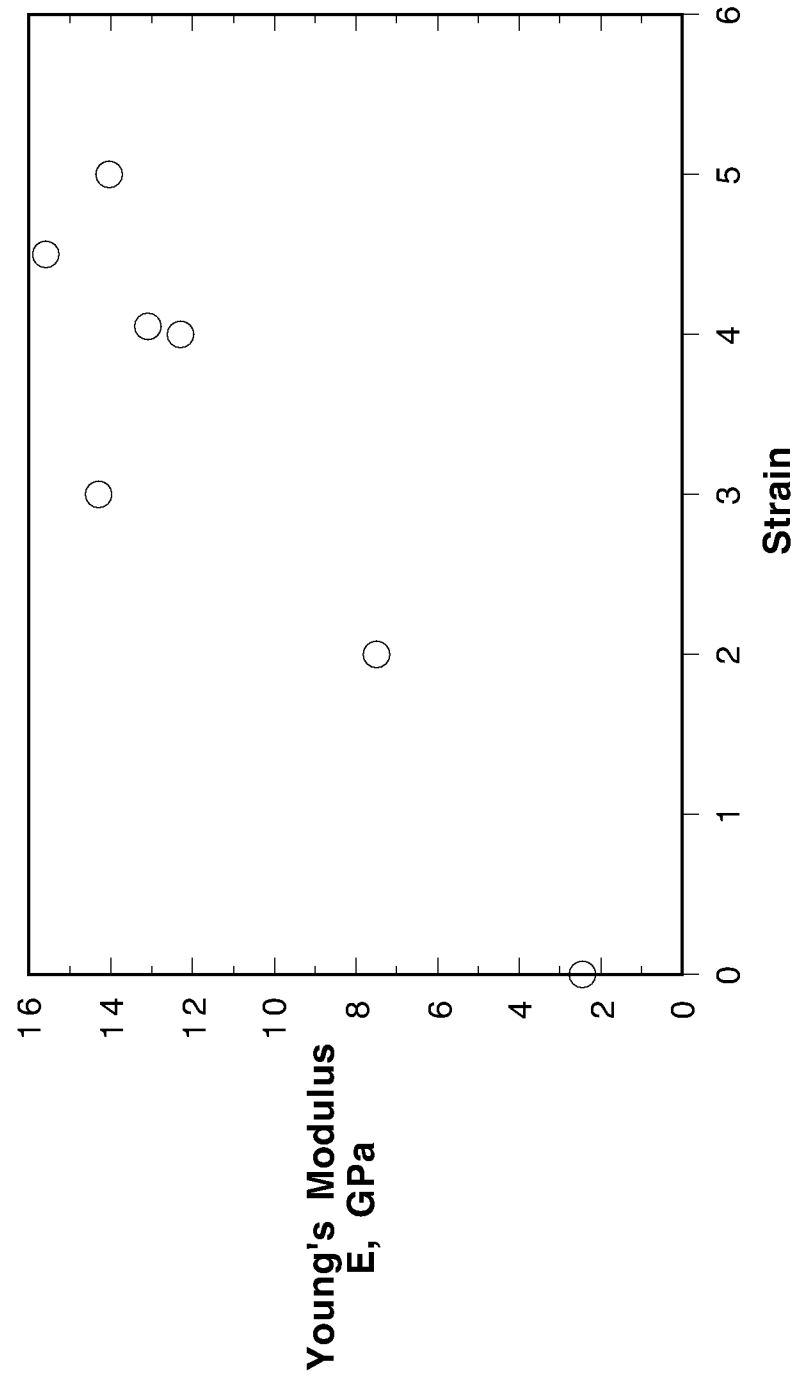Figure 3. Stress growth function (elongational viscosity) during uniaxial stretching of LaRC™-IA at 250°C.

Figure 4. Effect of strain achieved during 240°C stretch on room-temperature modulus of LaRC™-IAX.
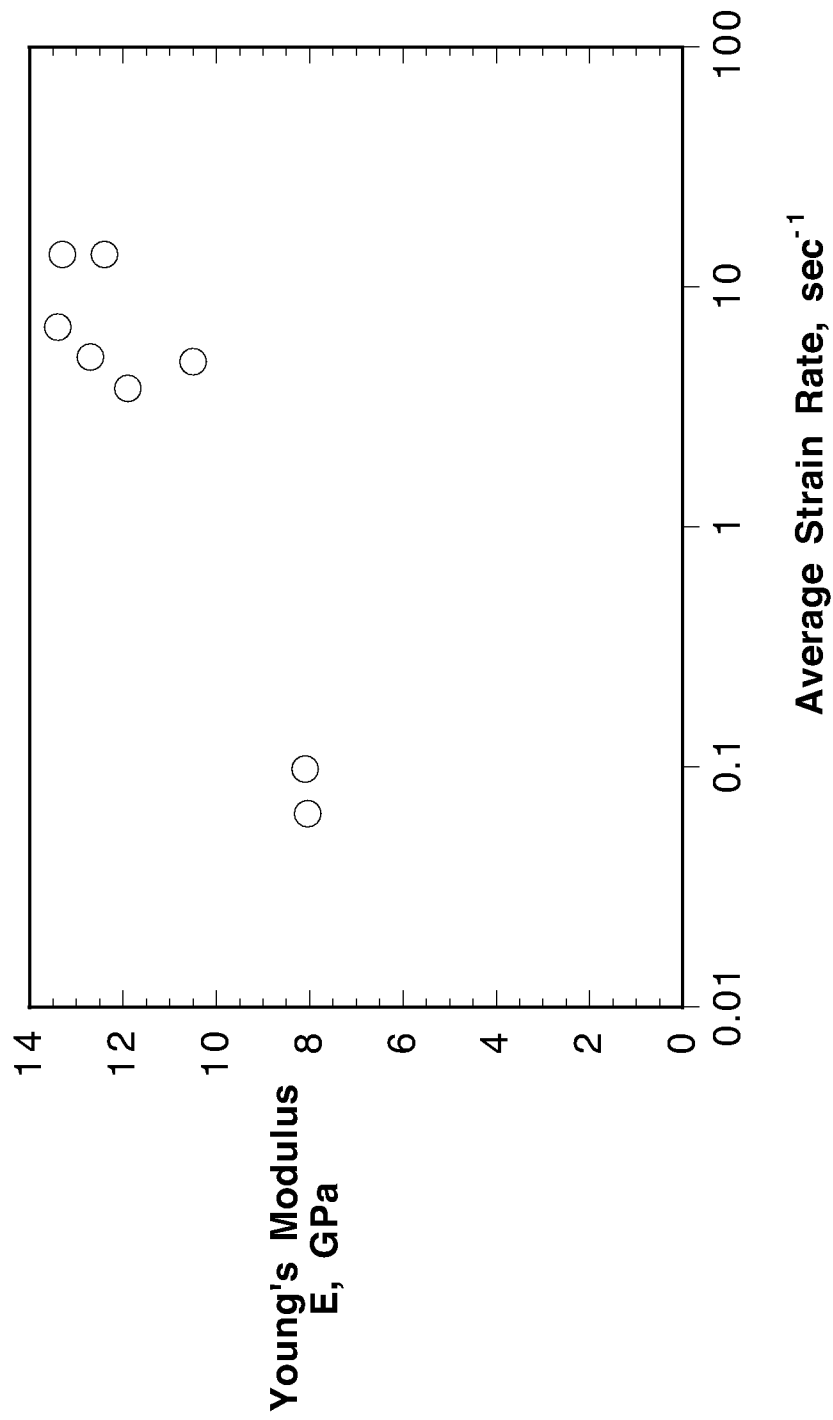
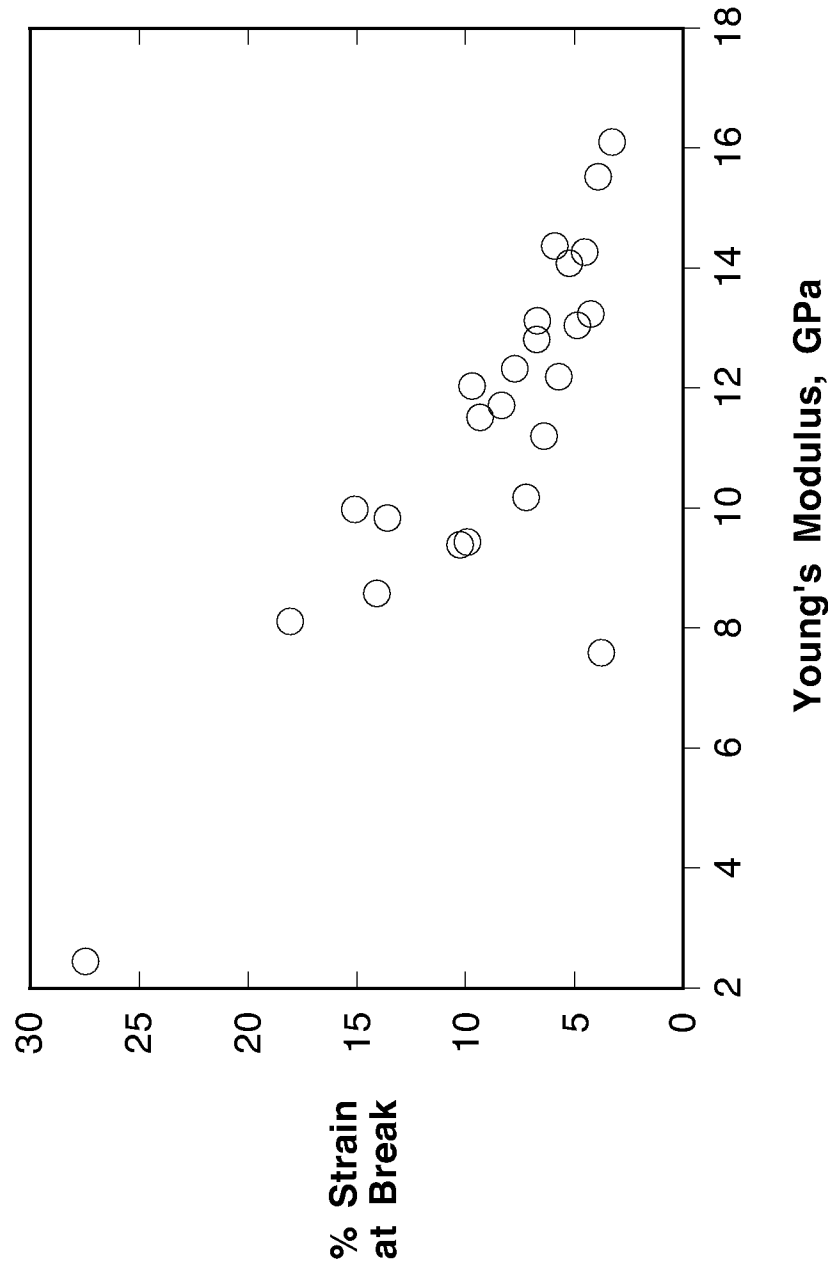Figure 5. Effect of strain rate during 260°C stretch on room-temperature modulus of LaRC™-IAX.

Figure 6. Relationship between modulus and breaking strain for LaRC^{TM}-IAX films prepared at a variety of stretching conditions.
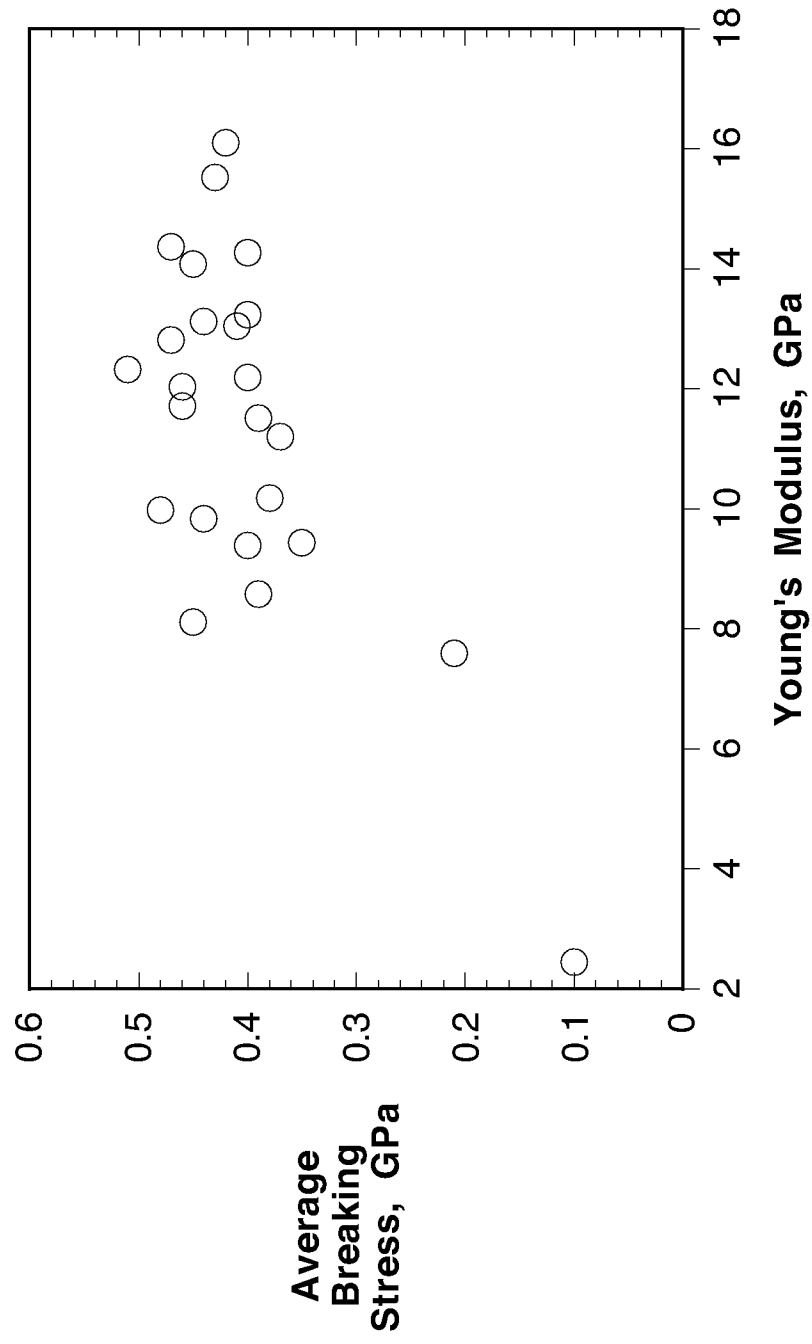
Figure 7. Tensile breaking stress of LaRC[TM]-IAX stretch-oriented films produced under a range of conditions.

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13. ABSTRACT (Maximum 200 words)

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